

Compression-Ignition Fuel Properties of Fischer-Tropsch Syncrude

G. J. Suppes,* J. G. Terry, M. L. Burkhart, and M. P. Cupps

Department of Chemical and Petroleum Engineering, The University of Kansas, 4006 Learned, Lawrence, Kansas 66045-2223

Fischer-Tropsch conversion of natural gas to liquid hydrocarbon fuel typically includes Fischer-Tropsch synthesis followed by refining (hydrocracking and distillation) of the syncrude into mostly diesel or kerosene with some naphtha (a feedstock for gasoline production). Refining is assumed necessary, possibly overlooking the exceptional fuel qualities of syncrude for more direct utilization as a compression-ignition (CI) fuel. This paper evaluates cetane number, viscosity, cloud-point, and pour-point properties of syncrude and blends of syncrude with blend stocks such as ethanol and diethyl ether. The results show that blends comprised primarily of syncrude are potentially good CI fuels, with pour-point temperature depression being the largest development obstacle. The resulting blends may provide a much-needed and affordable alternative CI fuel. Particularly good market opportunities exist with Environmental Policy Act (EPACT) applications.

Introduction

The world's natural gas reserves are about 5000 trillion cubic ft³. These reserves are about 20% less than crude oil reserves by energy, but they are located at different geographical regions and can be supplemented indefinitely with coal and biomass gasification. Therefore, technology that allows expanded and improved utilization of natural gas resources also provides long-term energy security for most of the world.

Development opportunities exist with the many large reserves of natural gas that are not being used to their full economic potential. This is especially true for remote or subquality reserves that comprise about half of the known reserves (Agee et al., 1996). Current methods for developing these remote or subquality reserves include methanol and ammonia production. These constitute markets that are considered to offer limited potential, and so Fischer-Tropsch synthesis is being considered as a method to convert these reserves into liquid fuels which can be more easily transported and which can better address vehicular fuel needs.

Syntroleum predicts syncrude costs of \$14–21/barrel (Agee et al., 1996). While these prices are only nominally competitive with crude oil, these syncrude prices (\$0.33–0.50/gal) are definitely less expensive than diesel distillate, which costs \$0.50–0.70/gal. Furthermore, syncrude is essentially free of sulfur, aromatics, metals, asphalt, and other contaminants commonly found in natural crude (Agee et al., 1996) and may have utility for more direct utilization to meet vehicular fuel needs. The most direct and low-cost method of syncrude utilization would avoid processing typically associated with refining—a very real possibility due to the superior quality of syncrude. By default, refinery-free processing would be limited to processing which can be performed at distributors and could include blending and additive addition.

The research of this paper evaluates advantages of blending light syncrude with ethanol, biodiesel, diethyl

ether, hexanes, and 87-octane gasoline. Light syncrude comprises most of the Fischer-Tropsch product mixture, with 90% (by mass) of the light syncrude composition having carbon numbers less than 20.

Pour-point temperature requirements were the most difficult to achieve, and so two additives (IU8092 and IU8094 of the Mid-Continental Chemical Co.) were evaluated for their effectiveness as pour-point depressants.

Flash-point temperatures were estimated. Ideal solution models showed that blending with ethanol, diethyl ether, or gasoline would lower flash-point temperatures to values lower than typically encountered with diesel. Since the blends may not meet flash-point temperature specifications, they may not be marketable as diesel in some markets; however, these blends potentially have exceptional performance as a fuel in diesel engines and should have receptive markets for use in diesel engines despite being marketed under a different name. Since the fuel would technically not be diesel, the engine should be referred to as a CI engine and the fuel as a CI fuel.

The primary goal of this research is to demonstrate that blending alone can be used to improve the most important CI application properties of syncrude. A fuel having a cetane number >45 and a pour-point temperature <−10 °C would meet the demands of many diesel markets. Ultimately, the use of blending and additives would give way to better, shape-selective catalysts that would produce syncrude that would require little or no blending. The proposed upgrading through blending and additive utilization would be a significant milestone toward sustainable Fischer-Tropsch commercialization.

Background

Fischer-Tropsch Synthesis. Syncrude production from natural gas is a two step procedure (Davies, 1997). First, natural gas is converted to synthesis gas (predominantly carbon monoxide, hydrogen, and sometimes nitrogen). Second, the synthesis gas is polymerized to hydrocarbon chains through Fischer-Tropsch reactions.

* To whom correspondence is to be addressed. Phone: 785-864-3864. Fax: 785-864-4967. E-mail: gsuppes@ukans.edu.

Table 1. Melting Points (mp) and Boiling Points (bp) of Several Straight-Chain Paraffins and 1-Alkene Olefins (Dean, 1985) [All Temperatures Are in °C]

	mp	bp		mp	bp
C _{6:0}	-95.3	68.7	C _{6:1}	-139.8	63.5
C _{10:0}	-29.8	174.1	C _{10:1}	-66.3	170.6
C _{14:0}	5.9	253.5	C _{14:1}	-12.9	251.2
C _{18:0}	28.2	316.7	C _{18:1}	17.7	314.9

This produces a waxy syncrude comprised mostly of saturated hydrocarbons with carbon numbers between 1 and 100. Light hydrocarbons can be easily stripped from the mixture and recycled in the Fischer-Tropsch process, leaving a product comprised mostly of C₄-C₂₀ hydrocarbons—a paraffin range leading to excellent CI fuel properties. Unfortunately, up to one-third of the product will be >C₂₀ and will tend to solidify at ambient temperatures (see Table 1).

Due to the waxy nature of Fischer-Tropsch syncrude, pour-point temperatures are a problem (Marano and Holder, 1997a,b). For use as vehicular fuel, the syncrude typically is hydrocracked and fractionated to diesel, kerosene, and naphtha (Schwartz, 1993).

Commonly considered routes toward commercialization include this additional refining step. Approaches toward utilization of syncrude without hydrocracking would need to address key fuel performance criteria such as pour-point and ignition properties. Production of light syncrude by separating the syncrude into a light syncrude (mostly <C₂₀) and a wax (mostly >C₂₀) could be performed at the Fischer-Tropsch facility and would provide a light syncrude product with better flow characteristics than the total product mixture. This light syncrude is liquid at ambient temperatures and could be used as a fuel without further refining. No published research is available on the CI fuel properties of this light syncrude.

Properties of Premium Diesel. The fuel industry in the United States is undergoing what could be described as a revolution in diesel fuel quality. Conoco, Citgo, and Mobil are expanding or planning to expand premium diesel product offerings (Peckman, 1997a,b; Callison, 1997). Most of the other major oil companies already have significant premium diesel programs.

Due to the fast growth of premium diesel utilization, the National Conference of Weights & Measures has acted to define "premium" diesel. Energy content, cetane number, fuel injector cleanliness, low-temperature operability, and thermal stability are the five properties identified with premium diesel (Peckman, 1998). Premium diesel fuels are expected to meet premium performance criteria in at least two of these five areas. Cetane numbers are considered by many to be the most important of these properties.

Cetane numbers >52 are relatively common in Europe and Japan, both of which are considered to have better quality diesel than the U.S. In the U.S. a >40 cetane number specification is in place, with average cetane numbers around 45. Benefits of higher cetane numbers include reduced NO_x, particulate matter, hydrocarbon, and carbon monoxide emissions as well as smoother engine operation (Beatrice et al., 1996; Bertoli et al., 1993; Mikkonen et al., 1997). Fischer-Tropsch-based diesel fuels could be marketed as premium products if high cetane numbers would be preserved during processing.

(a) **Pour-Point Depression.** Cloud-point and pour-point temperatures characterize the low-temperature

operability of diesel fuel. Recommended specifications vary depending on the geographic region and season in which the fuel is used. ASTM standards D-2500 and D-97 describe respective experimental procedures. In practice, the pour-point temperature is usually similar to the cold flow filterability temperature (ASTM standard D-4539).

Premium diesel fuels often have additives that lower the cloud and pour points of the fuel. This provides a better performance in cold weather. A typical premium winter-grade diesel fuel has a cloud point around -15 °C and a pour point of about -29 °C; however, such stringent specifications are not actually useful in warmer climates or during the summer. New premium diesel requirements will likely vary with location and season based on ASTM D-975 tenth percentile minimum ambient air temperature charts and maps.

Cloud-point temperatures correlate with the onset of freezing. When the temperature is lowered, the small crystals cause a cloudy appearance. At pour-point temperatures, flow essentially ceases due to the buildup of solids. Crystal morphology has a significant impact on the pour points of mixtures. For pure components, pour-point and cloud-point temperatures are equal to the freezing point of the pure substance. Methods of reducing pour points without significantly changing the fuel composition involve the use of polymer additives that change the crystals' morphologies and/or sizes (Botros, 1997). Additives cause smaller crystals to form either by creating additional nucleation sites or by interfering with crystal surfaces and growth.

Reducing the fraction of high carbon number paraffins will also reduce pour-point temperatures. Changes in composition can be achieved by hydrocracking the larger molecules or by diluting the paraffins through blending. For both approaches, the compositions of the waxy components are reduced.

Diesel fuel contains many components that are solids at ambient or near-ambient conditions. Thus, the underlying thermodynamics (driving force) for crystal formation in mixtures is described by theory developed for freezing point depression, as presented in eq 1 (Sandler, 1989) where γ_i is the activity coefficient of

$$\ln \gamma_i x_i = - \frac{\Delta H^{fus}(T_m)}{R} \left[\frac{T_m - T_f}{T_m T_f} \right] - \frac{\Delta C_p}{R} \left[1 - \frac{T_m}{T_f} + \ln \left(\frac{T_m}{T_f} \right) \right] \quad (1)$$

component i (waxy component), x_i is the mole fraction of component i , ΔH^{fus} is the heat of fusion for the waxy component i , ΔC_p is the heat capacity of liquid i minus the heat capacity of solid i , T_m is the normal melting point of pure component i , T_f is the temperature where i solidifies in the mixture.

Equation 1 describes how freezing point depression ($T_m - T_f$) is related to several pure-component properties of the component having the propensity to freeze (waxy component) as well as two mixture properties (the mole fraction and activity coefficient of the waxy component in the liquid mixture). Decreases in either the mole fraction or activity coefficient of the waxy component will lead to greater freezing point depression.

Both hydrocracking and blending reduce the mole fractions of the waxy components. Furthermore, when

blending with a fixed mass fraction of another fuel (e.g., ethanol or gasoline), it is potentially advantageous to choose a fuel with a lower molecular weight, leading to a greater reduction of the mole fraction of the waxy component in the mixture. However, if the smaller size of the blending fuel also leads to increased solution nonidealities (i.e., increased activity coefficients), the use of some lower molecular weight blend stocks may not reach their expected potential.

(b) **Viscosity of Mixtures.** The viscosity of a diesel fuel is important to the performance of fuel injection equipment. Diesel fuel injection systems are designed with very low tolerances and are easily affected by fuel viscosity. If the fuel is too viscous, a cold environment will affect the way it is atomized by an injector. Also, when the fuel is hot, inadequate viscosity can cause leakage of fuel around the injector's plunger, leading to severe power loss. The standard kinematic viscosity range for diesel fuels is 1.9–4.1 mm²/s at 40 °C. Premium diesel fuels usually are sold as either a summer blend or a winter blend. The viscosity of a winter blend diesel fuel will typically be lower than that of a summer blend so as to provide the same viscosity at the temperatures of application.

(c) **Cetane Number Characterization.** The cetane number of a diesel fuel is a measure of ignition quality. A higher cetane number indicates that the ignition delay time will be shorter. This results in easier engine startup, smoother engine operation, less engine noise, and more complete combustion, thereby reducing emissions. However, if the cetane number is too high, the fuel could ignite before proper fuel–air mixing is allowed to occur; this could increase exhaust emissions. Injector timing should be optimized with the fuel's cetane number for optimal performance.

(d) **Flash Points.** Flash-point temperatures are a measure of the propensity for a fuel to ignite when exposed to a flame or ignition source. Clothier et al. (1993) report the approximate boiling ranges of gasoline and diesel to be 30–200 and 160–330 °C, respectively. The lower ends of these ranges (i.e., the vapor pressures of hydrocarbons) tend to correlate with typical flash-point temperatures of <–40 °C for gasoline and >38 °C (>56 °C in some European countries) for diesel.

Due to safety and fugitive emissions considerations, it is clearly desirable to use fuels with higher flash-point temperatures. However, the widespread acceptability of using fuels with flash-point temperatures <–40 °C (widespread use of gasoline) suggests that flash-point specifications are not as important as other CI fuel properties for vehicular applications.

For mixtures of C₈₊ syncrudes with gasoline, gasoline would dominate gas-phase compositions at flash-point temperatures. Equation 2 uses Raoult's law and the

$$\frac{T_1}{T_2} = 1 + \frac{T_1 R \ln(x)}{\Delta H} \quad (2)$$

Clausius–Clapeyron equation to estimate increases in flash-point temperatures due to reductions in composition of the light component. T_2 is the temperature where the diluted light component (at mass fraction x) will provide the same vapor pressure as the neat light component at temperature T_1 . T_1 is the flash-point temperature of the pure light component (e.g., 230 K), T_2 is the flash-point temperature of the mixture, R is the ideal gas constant (e.g., 8.314 J/mol/K), x is the mole

fraction of the light component in the mixture, and ΔH is the enthalpy of vaporization of the light component (e.g., 26 kJ/mol).

Markets for Fischer–Tropsch Fuels. The goals of many Fischer–Tropsch projects are to indirectly compete in the large diesel and gasoline fuel markets (Schwartz, 1993). For these markets, the price of the final product will largely determine market penetration. When competing with crude oil, Fischer–Tropsch syncrudes may bring a premium price due to their ability to be reformed at high yields to valuable components of gasoline and diesel.

Since fuels based on >70% Fischer–Tropsch syncrude largely would not be derived from natural crude oil, these CI engine fuels should fulfill EPACT requirements. They would fill an important niche in the EPACT fuel menu, namely, an affordable liquid fuel that can be used in conventional diesel engines. In addition, Fischer–Tropsch fuels generally have high cetane numbers (>65) and near-zero aromatic contents—both leading to emissions reductions for properly tuned CI engines.

EPACT is an acronym for the U.S.'s Environmental Policy Act that promotes, and in some cases mandates, the use of fuels other than petroleum-derived gasoline or diesel. For SI engines, a number of good alternative fuels exist, including propane, natural gas, ethanol, and methanol. However, the most prominent alternative fuel for CI engines is biodiesel that sells for >\$3.00/gal. Due to the high price of biodiesel, most experts do not perceive a good EPACT alternative to diesel to be available. Market opportunities exist for affordable, synthetic diesel fuels in EPACT applications involving small trucks, vans, sports utility vehicles, and city buses.

Experimental Systems

A Fischer–Tropsch diesel and Fischer–Tropsch syncrude were evaluated for their suitability as CI fuels.

The fuel properties tested were cetane number, kinematic viscosity, cloud point, and pour point. Calculations were performed using eq 2 to estimate the impact of gasoline addition on the flash-point temperature of the mixture with light syncrude.

To improve these properties of the light syncrude, tests were performed on blends of the light syncrude with ethanol, hexanes, diethyl ether, biodiesel, and 87-octane gasoline. With the exception of hexanes, these mixtures are of interest to determine if the light syncrude can be utilized by blending it with these common blend stocks without further refining. The mixtures with hexanes were useful in providing fundamental insight into performance trends.

Cetane Number. The cetane number is a measure of a fuel's ignition quality. High cetane numbers correspond to low ignition delay times (better ignition quality). Ignition delay times are known to correlate well with cetane numbers. During the present study the ignition delay times were directly measured in contrast to using a cetane engine. Ignition delay time data have the advantage of providing more fundamental information to assist in interpreting data trends. A detailed description of the equipment can be found elsewhere (Suppes et al., 1997a,b). Allard et al. (1996, 1997) detail preferred operating procedures for constant volume combustors.

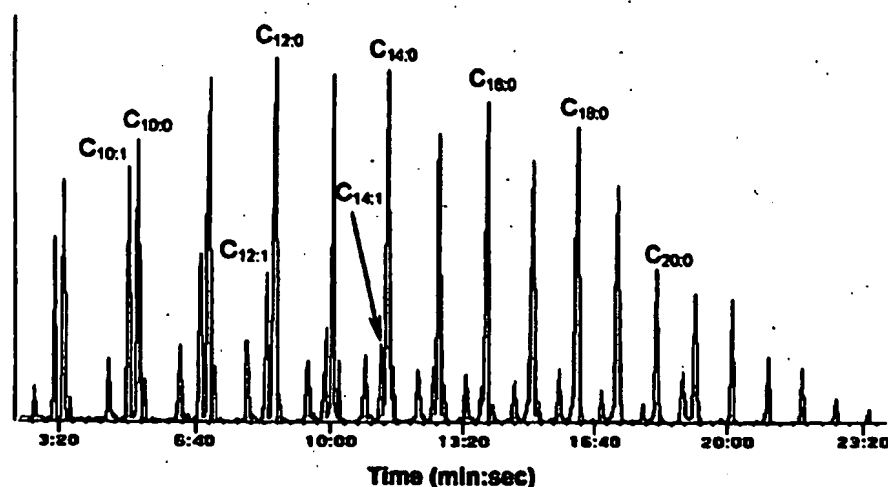


Figure 1. GC-MS analysis of light syncrude.

To determine the cetane number of the test fuels, ignition delay time results were compared to data from U-13 and T-20 reference fuels. Three mixtures were used, corresponding to cetane numbers of 30.0, 45.3, and 60.1. The tests were carried out at temperatures of 750, 800, and 833 or 850 K. Approximately six ignition delay times were measured at each temperature.

Thompson et al. (1997) conducted an extensive study of cetane number estimation methods. They found that the recommended ASTM D-613 cetane number method had repeatabilities and reproducibilities that steadily increased with the value of the cetane number being measured. A cetane number of 40 would typically have a repeatability and reproducibility of 0.8 and 2.8, while a cetane number of 56 would have respective values of 0.9 and 4.8.

Although ignition delay times were measured at three temperatures, only the 800 K data were used to estimate cetane numbers. Standard deviations are reported for the 800 K data. Since six measurements typically were taken at 800 K, the 95% confidence interval is about 0.8 times the reported standard deviations. These 95% confidence intervals were typically between corresponding repeatability and reproducibility values reported by Thompson et al. (1997).

Kinematic Viscosity. The kinematic viscosities of test fuels were tested by ASTM standard D-445 using a Cannon-Fenske Routine size 50 capillary viscometer. The kinematic viscosity of each fuel was measured at 40 °C.

Cloud-Point and Pour-Point Measurements. The cloud point is related to the temperature when the fuel begins to form wax crystals, causing a cloudy appearance in the mixture. A FTS Systems chiller capable of controlled bath temperatures down to -80 °C was used to gradually lower the temperature of the test fuel until the cloud point was reached. ASTM standard D-2500 (cloud point) and D-97 (pour point) procedures were followed with the exception that 5-mL vials were used rather than 100-mL beakers due to the limited supply of syncrude. Since the relatively small test samples would experience greater wall effects than the recommended 100-mL samples, the pour-point values may be slightly high.

Fuel Sources. (a) Fischer-Tropsch Samples. The synthetic distillate and light syncrude samples were

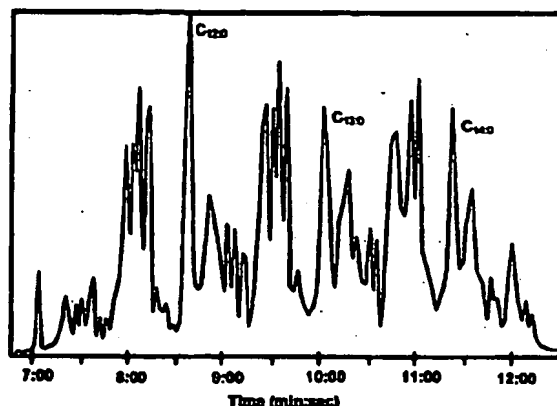


Figure 2. GC-MS analysis of light syncrude diesel distillate.

provided by Syntroleum of Tulsa, OK. The light syncrude is a fraction of a Fischer-Tropsch product that was separated from the waxy components by a method that would be viable at syncrude production facilities. The distillate is a fraction of the light syncrude. Neither product has been hydrocracked.

A gas chromatograph equipped with a mass spectrometer detector (GC-MS) was used to determine product distributions for both the light syncrude and the distillate. The GC-MS chromatographs are shown by Figures 1 and 2, respectively.

The largest peak of the light syncrude is at 8 min and 30 s and corresponds to a straight-chain, $C_{12:0}$ paraffin. Immediately to the left and approximately one-third in magnitude of the $C_{12:0}$ paraffin peak is the corresponding $C_{12:1}$ olefin peak. This pairing is consistent throughout the chromatograph starting at about 3 min and 20 s for $C_{9:0}$ and $C_{9:1}$ and rapidly tapering off at 22 min and 30 s with the $C_{24:0}$ peak.

The chromatograph of the distillate (Figure 2) is more difficult to interpret, possibly due to oxidation which occurred during fractionation (such oxidation would be largely eliminated upon scale-up). $C_{12:0}$, $C_{13:0}$, and $C_{14:0}$ paraffins and various oxygenated forms (including alcohols) of these species dominate the distillate composition.

(b) Other Chemicals. Ethanol, diethyl ether, biodiesel, hexanes, and gasoline were used as blend stocks to

Table 2. Cloud- and Pour-Point Temperatures of Test Fuels [All Temperatures Are in °C]

	cloud point	pour point		cloud point	pour point
regular diesel	-10	-13	light syncrude/gasoline		
synthetic diesel distillate	-50	-54	% gasoline (87 octane)		
light syncrude	6.5	2	30	-2	-6
light syncrude/EtOH			30% gas with pour-point depressant		
% EtOH			UI8092 at 130 ppm	-2	-9
10	6.5	3	UI8092 at 320 ppm	-2	-17
20	6.5	2	UI8092 at 520 ppm	-2	-19
30	6.5	3	UI8092 at 950 ppm	-2	-21
biodiesel	-4	-6	UI8094 at 150 ppm	-2	-8
			UI8094 at 240 ppm	-2	-12
light syncrude/biodiesel			UI8094 at 460 ppm	-2	-18
% biodiesel			UI8094 at 850 ppm	-2	-21
10	5	1	light syncrude/hexanes		
20	4	0	% hexanes		
30	4	0	30	-3	-12
light syncrude/biodiesel/EtOH			light syncrude/diethyl ether		
80/10/10	5	1	% diethyl ether		
70/10/20	5	2	30	-2	at -10 °C
70/20/10	5	2			solids settled

dilute light syncrude. Ethanol and diethyl ether were purchased in bulk at purities >99.8%. The biodiesel is a methyl ester of soybean oil and was donated by the National Biodiesel Board. HPLC-grade hexanes were purchased from Aldrich. The 87-octane gasoline was purchased locally. The diesel was supplied by a distributor and is a summer grade of low cetane quality. The pour-point depressants were donated by the Mid-Continental Chemical Co.

Experimental Data

Properties of Fischer-Tropsch Crude and Distillate. The experimental data were measured for several mixtures of light syncrude, synthetic diesel, and reference fuels. The impact of mixing on cloud-point and pour-point temperatures, kinematic viscosities, and cetane numbers was evaluated and reported in Table 2.

The pour-point data of Table 2 show the light syncrude to have unacceptably high cloud-point and pour-point temperatures of 6.5 and 2 °C. Various fuels were mixed with the synthetic crude to attempt to reduce the values of the pour-point temperatures. Biodiesel, ethanol, and diethyl ether were largely ineffective for reducing pour points. The hexanes were effective, and gasoline was moderately effective.

Since gasoline is the least expensive of the blend stocks, its mixtures were chosen for further studies with pour-point depressants UI8092 and UI8094.

Viscosities were measured at 40 °C and are reported in Table 3. Both the synthetic diesel and the synthetic crude are within ASTM guidelines with viscosities of 1.9 and 2.3 mm²/s, respectively. A 30% mixture of ethanol with light syncrude results in a viscosity slightly lower than the diesel specification. The viscosity of the 30% blend with gasoline is too low.

Figure 3 shows the correlation of cetane number versus ignition delay time at three different temperatures. The curve was prepared with mixtures of Phillips' U-13 and T-20 test fuels. Such correlations are considered valid for a period of about 2 weeks when the data are evaluated by the same researcher. It is

Table 3. Kinematic Viscosities (mm²/s) of Test Fuels at 40 °C

fuel	kinematic viscosity (mm ² /s)
regular farmland diesel	3.05
synthetic diesel distillate	1.92
light syncrude	2.32
light syncrude/EtOH	
% EtOH	
10	2.21
20	2.06
30	1.78
syncrude/gasoline 70/30	1.28
gasoline	0.48
EtOH	1.00

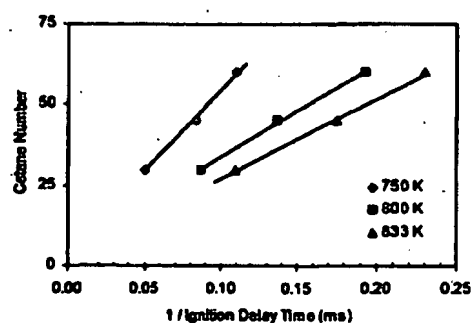


Figure 3. Ignition delay time (ms) versus cetane number of the T-20 and U-13 reference fuel mixtures.

common for reproducibility errors to be >2.8 cetane numbers (Henly, 1997) when using ASTM D-613 evaluation methods—for this reason, periodic comparison to reference fuels is recommended when evaluating cetane numbers.

For these data, the cetane numbers are approximately proportional to the reciprocal ignition delay times. Linear regression was performed at 750, 800, and 833 K. The respective R^2 values for the best-fit curves for these data were 0.997, 0.998, and 0.999; however, despite the good correlations, errors of up to 0.5CN were produced from the correlation alone. This error was eliminated by using the three-constant, calibration

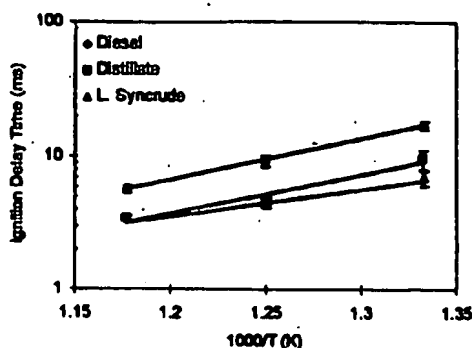


Figure 4. Ignition delay times of summer diesel, syncrude diesel distillate, and light syncrude.

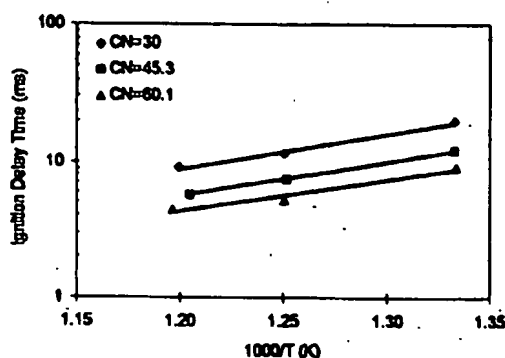


Figure 5. Arrhenius-type plot of ignition delay time for Phillips' reference fuels.

equation given by eq 3 for data at 800 K where CN is

$$CN = -17.2 + 215/t_d^{0.62} \quad (3)$$

cetane number and t_d is ignition delay time in millisecond.

Figure 4 summarizes ignition delay time data for the Fischer-Tropsch products. The slopes of the best-fit lines of Figure 4 are interpreted as being the activation energy for the overall ignition process (Ryan and Stapper, 1987). The estimate of the cetane number depends on both the best-fit slope and the temperature where the test fuel is compared to the reference fuels. Comparisons at temperatures with ignition delay times between 2.5 and 3.0 ms are preferred since the ASTM D-613 test procedure measurements occur at ignition delay times of about 2.5 ms. For interpreting the present data 800 K was used. Within the standard deviations, the 800 K measurements are representative of the data set over all temperatures.

Figure 5 shows the Arrhenius-type plots for the reference fuels. The linearity of the plots illustrates the consistency of the data as well as the Arrhenius-type behavior. However, it appears that, for the reference fuels as well as most of the data, the 800 K data have a slight negative deviation from Arrhenius-type behavior. At ignition delay times between 1.5 and 10 ms, the ignition process goes from a gas-phase, reaction-kinetics-limiting reaction to a heat-transfer-limiting process (fuel evaporation). This would explain why the 800 K data are typically lower than the straight-line regressions. During this transition, the ignition delay times of liquid fuels approach asymptotic values between 1.0 and 1.5 ms. Since these trends are observed for the

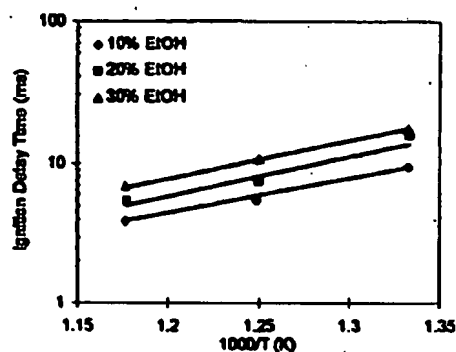


Figure 6. Impact of ethanol on ignition delay times of light syncrude.

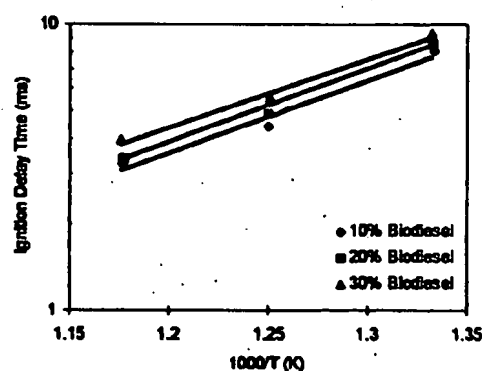


Figure 7. Impact of biodiesel on ignition delay times of light syncrude.

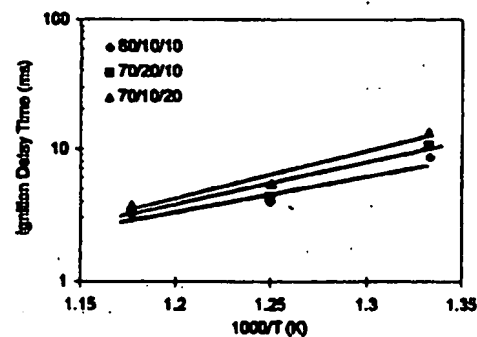


Figure 8. Impact of both ethanol and biodiesel on ignition delay time of light syncrude. Direct comparison to light syncrude and a 60.1 cetane number (CN) reference sample illustrates relative performances. Ratios are masses of light syncrude, biodiesel, and ethanol, respectively.

reference fuels as well as the fuels being evaluated, the systematic errors cancel.

Figures 6–9 present similar, Arrhenius-type plots for mixtures of the light syncrude with ethanol, biodiesel, and gasoline. Table 4 summarizes ignition delay time data at 800 K with standard deviations and cetane numbers as estimated by eq 3.

The synthetic diesel (syncrude distillate) has a cetane number of 65.3 ± 2.4 , which is slightly lower than the light syncrude, which has a cetane number of 69 ± 4.8 . The synthetic fuels display impressively high cetane numbers, sufficiently high to allow blending with low cetane blend stocks to improve pour points. When light syncrude is blended with a blend stock of lower cetane

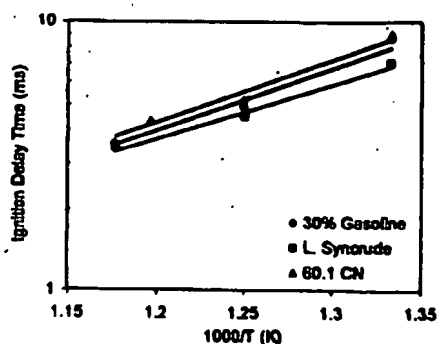


Figure 9. Impact of gasoline on ignition delay time of light syncrude. The 60.1 cetane number (CN) reference is superimposed for comparison.

Table 4. Calculated Numbers of Test Fuels Based on T and U Reference Fuels*

	T (K)	delay t (ms)	std (ms)	CN calc.	calc. std (CN)
Standards and Test Fuels					
30 CN	800	11.5	0.47	30.0	1.2
45.3 CN	799	7.3	0.51	45.3	2.6
60.1 CN	800	5.2	0.17	60.2	1.5
diesel	800	9.3	0.86	36.9	2.9
syncrude distillate	800	4.8	0.20	64.3	2.0
L syncrude	800	4.5	0.37	67.4	4.0
Ethanol Mixtures (% Ethanol Indicated)					
10%	801	5.5	0.31	57.9	2.5
20%	800	7.4	0.82	45.1	3.9
30%	800	10.6	1.23	32.5	3.3
Biodiesel Mixtures (% Biodiesel Indicated)					
10%	800	4.4	0.54	68.6	5.9
20%	800	4.9	0.72	63.5	6.6
30%	799	5.6	0.52	57.0	4.0
Gasoline Mixture (% Gasoline Indicated)					
30%	800	4.9	0.26	63.3	2.5
Light Syncrude/Biodiesel/Ethanol					
80/10/10	800	4.0	0.24	73.4	3.2
70/20/10	800	4.3	0.27	69.6	3.2
70/10/20	800	5.4	0.37	58.4	3.0

* All mixtures are with light syncrude and percentages in mass %. Standard deviations (std) are based on 800 K data.

number, the resulting blend typically has a lower cetane number than the light syncrude. This occurs when ethanol blend stock is added to the light syncrude, as illustrated in Figure 6. Cetane numbers generally approach values that are linear with composition; the biodiesel blends were atypical.

Discussion

Performance of Light Syncrude Blends. The light syncrude has a cloud point of 6.5 °C and a pour point of 2 °C, both unacceptably high. Pour-point temperatures were identified as the critical performance property that must be improved to use the crude product as a CI engine fuel in most markets. Fortunately, the ignition properties (cetane numbers) of the light syncrude are exceptional and allow blending as a method of freezing point depression. The high cetane number of the light syncrude compensates for the low cetane numbers of low-carbon-number blend stocks. Since low carbon numbers correlate with low cetane numbers (Owen and Coley, 1995), blending stocks which provide the maximum reduction in mole fraction of the waxy

components per mass of blend stock add-mix inadvertently have an adverse impact on cetane numbers.

Ethanol blend stock had no effect on the low-temperature properties even when applied at a 30% add-mix. The nonidealities that exist between ethanol and syncrude must lead to high activity coefficients for both components; these high activity coefficients ultimately diminish potential advantages associated with reducing the concentrations of the waxy components.

Diethyl ether lowered the mixture cloud-point temperature from +6.5 to -2 °C. However, when the mixture was further cooled, the solids settled out of the solution, as compared to the typical solid-liquid gel. This phenomenon can be attributed to the low density of diethyl ether (0.708) as compared to the density of the precipitating solids (>0.80). Reductions of the cloud-point temperatures would correctly be interpreted as true solvating phenomena.

Biodiesel lowered the cloud-point and pour-point temperatures of the light syncrude. The most significant benefit was at 20% biodiesel, where the cloud-point temperature was lowered to 4 °C and the pour-point temperature was lowered to 0 °C. Further addition of biodiesel to 30% had little effect. Biodiesel has a relatively large molecular weight, and so minimal improvements were expected.

Hexanes were the most effective for lowering the cloud-point and pour-point temperatures of the light syncrude. Hexanes, at 30%, lowered the cloud point of the syncrude from +6.5 to -3 °C and the pour point from +2 to -12 °C. The effect of hexanes on the low-temperature properties indicates that addition of naphtha or kerosene fractions may also be a good option.

Gasoline also lowered the cloud and pour points of the mixture. The mixture cloud-point and pour-point temperatures were -2 and -6 °C. Gasoline was about 60% as effective as hexanes. The poorer performance of gasoline could be attributed to the high molecular weights of certain gasoline components (leading to less of an impact on mixture mole fractions of waxy components) and possible nonidealities of aromatic-paraffin interactions (leading to higher activity coefficients).

Pour-point depressants were evaluated only in gasoline and added to the reductions in pour-point temperature achieved with 30% addition of gasoline. Treatment at rates of <0.1% led to pour-point temperatures of -21 °C in the 30% gasoline mixtures. Treatment at these rates would typically cost less than \$0.005/gal and is a viable option. The type of additive did not have a significant impact on performance. Also, at concentrations of 0.095%, reductions in pour points were only marginally better than those at 0.055%. The point of diminishing returns on pour-point depressants is apparently reached at a pour-point depression of about -15 °C. To achieve pour-point temperatures of <-15 °C will likely require the use of both blend stock and additives. The pour-point depressants had no impact on the cloud points, indicating that the additives impacted crystal growth but not the underlying thermodynamics.

With a pour-point temperature of -21 °C, the mixture containing 70% light syncrude, 30% gasoline, and 0.095% pour-point depressants has acceptable pour-point temperatures for many regions of the country. These pour-point temperatures could also be lowered by the addition of more gasoline to provide blends suitable for most CI fuel markets. In addition, with a

cetane number of 64, these fuels are likely to have exceptional performance characteristics for applications with injectors that can handle the lower viscosities.

The viscosity of the synthetic fuels is lowered by the addition of components with lower molecular weights such as ethanol. As ethanol was added, the viscosity was reduced from 3.05 mm²/s at pure syncrude to 2.05 mm²/s at 10%. Additional blending leads to unacceptably low viscosities.

The EPACT Fuels' Market. Mixtures of 30% gasoline with 70% light syncrude can be formulated to have acceptable pour-point temperatures (−21 °C) and exceptional cetane numbers (63.3). Preliminary economic analysis suggests that these fuels can be produced for less than the going rates for diesel fuel. However, further testing is needed since the cetane number is only an indication of the propensity for the fuel to ignite and work in a diesel engine. In particular, extended engine tests are warranted.

The high carbon number constituents of light syncrude could lead to problems with engine seizure or hydrocarbon emissions. Vegetable oils with carbon numbers near 60 are known to lead to buildup of tars in engine cylinders when used at concentrations of 20% in diesel. This is due to incomplete combustion and would thus also lead to relatively high hydrocarbon emissions. In the event that incomplete combustion of the higher carbon number constituents is a problem, it may be correctable with high engine compression ratios (increasing combustion temperatures) and high injector pressures (improving atomization).

In the event that light syncrude would not be economically competitive with diesel, fuels blended from light syncrude would likely still be competitive in the EPACT fuels' market. Ethanol is one of the most cost-effective fuels in the EPACT market at a production cost of about \$1.80/equivalent gasoline gal. Ethanol is used in SI engines using modified fuel systems which cost about \$700 more to produce. A blended syncrude could be used in diesel engines at efficiencies of 30–50% better than those realized with SI engines. If these blended syncrude fuels could be used in unmodified diesel engines, they would likely be the best available EPACT option.

Flash-Point Calculations. While blends of light syncrude with gasoline are expected to have exceptional performance characteristics, the flash points would be considerably lower than normal diesel. Equation 2 was used to estimate flash-point temperatures based on a mixture where the syncrude has an average molecular weight 2.5 times that of the light component. Values of $T_1 = 230$ K and $\Delta H = 26$ kJ/mol were used to estimate gasoline's physical properties. The ratios of T_1 to T_2 were calculated for several compositions. At gasoline mass fractions of 0.1, 0.2, and 0.3, the flash-point temperatures of the mixtures were estimated to increase by 30, 18, and 12 °C, respectively, above gasoline's flash point of −43 °C. Even at the lowest concentration, a typical flash-point temperature of diesel at >38 °C would be decreased to <−10 °C. This could create problems for some applications. Fuel storage and transport in itself would not be a problem since gasoline, which has an even lower flash point, is widely used and accepted as a vehicular fuel. However, the practice of using diesel fuel circulation to cool the injector may not be compatible with low-flash-point fuels. Fuel circulation through hot injectors has the potential of heating

fuels to conditions where low flash points can lead to explosion or fire.

Performance of Syncrude Diesel. The synthetic diesel distillate has a remarkably low cloud-point temperature at −50 °C and a pour point of −54 °C. Based on the melting point data of Table 1, such low pour-point temperatures would not be expected for a C₁₂–C₁₄ Fischer–Tropsch distillate comprised solely of hydrocarbons (Marano and Holder, 1997b). For comparison, Schaberg et al. (1997) report a pour-point temperature of −43 °C for Sasol's Fischer–Tropsch diesel distillates. Apparently, melting point depression in the absence of >C₁₅ products has a larger impact than expected. The differences between these two distillates is likely due to oxygenates present in the syntroleum product (see Figure 2).

Diesel distillates of syncrude are known to have excellent fuel performance characteristics. These studies show the distillate to have a high cetane number at 64.3 ± 2.0 . This compares to typically reported values of >70 for Fischer–Tropsch syncrude diesels. Based on the GC-MS chromatographs of Figures 1 and 2, this performance is likely also due to oxygenates generated during fractionation of the syncrude. Such oxidation would not be expected for larger scale fractionation and has not been observed for products produced from hydrocracked Fischer–Tropsch syncrude.

Cetane Number Estimation and Relative Performance. Estimates of the cetane numbers are presented in Table 4. These estimates were based on ignition delay time measurements. Typical Arrhenius-type behavior was observed for every fuel.

As expected, the addition of ethanol markedly lowers the cetane numbers of the light syncrude. Even at 20% ethanol, the cetane number barely meets performance expectations for diesel fuels. The impact of ethanol on mixture cetane numbers would be expected to level off and asymptotically approach a value of about 12 for neat ethanol. Due to both the adverse impact on cetane numbers and ineffectiveness as a pour-point depressant, ethanol may not be a good option.

When both biodiesel and ethanol blend stocks were used, ethanol had less of an adverse effect on cetane numbers. The increase in cetane number due to the addition of 10% biodiesel to the light syncrude was unexpected. Neat biodiesel will typically have a cetane number between 48 and 52 but may range from 45 to 55 depending upon the extent of peroxide buildup and the production method (Gerpen et al., 1997). Biodiesel could exhibit a cetane-related synergy at lower concentrations when mixed with light syncrude due to interactions between the peroxides and light syncrude; however, definite trends cannot be discerned when considering the standard deviations of the cetane number estimates. In any case, little performance advantage is realized when increasing the cetane number from 65 to 70 (unlike the real benefits associated with increasing the cetane number from 45 to 50).

Miscibility of Ethanol and Diethyl Ether. Based on the comparison of several different models capable of predicting liquid–liquid equilibrium, Walas (1986) showed that liquid–liquid phase behavior typically occurs when infinite-dilution activity coefficients exceed 12. UNIFAC predicts the infinite-dilution activity coefficients of ethanol and diethyl ether in dodecane as 28 and 1.1 at 10 °C. For diethyl ether, liquid–liquid miscibility problems are neither predicted nor observed.

However, UNIFAC predicts miscibility problems for the ethanol system, contrary to experimental observations. For this reason, the phase behavior of the ethanol-syncrude system was investigated further.

Further investigation revealed that a transient second liquid phase formed when the suspended solids melted in the ethanol-syncrude mixture. The solid phases are concentrated in the higher carbon number paraffins, and, apparently, immiscible liquid droplets form due to these high carbon number paraffins repelling the continuous phase which contains large amounts of ethanol. This phenomenon is only temporary with the essentially pure paraffin droplets rapidly diffusing back into the continuous liquid phase. Ethanol-syncrude mixtures are likely on the verge of forming two liquid phases that are thermodynamically stable. Low concentrations of water would likely instigate the formation of a second phase.

Conclusions

The suitability of C_9 - C_{22} Fischer-Tropsch light syn crude and diesel distillate were evaluated for use as blending components for CI fuels. The syn crude diesel distillate showed exceptional cetane number and pour-point temperature characteristics, but the light syn crude exhibited a high pour-point temperature at 2 °C. While the results of this study are specific to the C_9 - C_{22} Fischer-Tropsch light syn crude, the results provide insight into general performance trends of Fischer-Tropsch light syncrudes.

Of the fuels blended with light syn crude, only gasoline and hexanes were effective in reducing pour-point temperatures to acceptable levels. Ethanol was not effective due to solution nonidealities, leading to higher activity coefficients that diminished potential freezing point depression. Diethyl ether provided good cloud-point depression; however, its low density led to problems associated with solids settling out of the solution. Biodiesel lowered the pour points; however, its impact was minimal due to the high molecular weight of biodiesel.

Fuel blends comprised of 70% syn crude, 30% gasoline, and 0.05% pour-point depressant exhibited excellent fuel properties, including a cetane number of about 63 and pour-point temperatures < -18 °C. This or similar blends will likely have low viscosities and low flash-point temperatures as compared to diesel fuel. The low flash-point temperatures of these fuels suggest that preferred applications would be with fuel systems that do not use fuel circulation to cool the injector. Several engine manufacturers have manufactured diesel engines powered by ethanol and methanol. These engines have overcome problems with low flash point fuels (Weuben et al., 1990).

Engine tests are recommended to identify those operating parameters that would eliminate possible problems due to incomplete combustion of the high-carbon-number components of the light syn crude.

Acknowledgment

The synthetic distillate and light syn crude samples used for these studies were provided by Syntroleum; their support is greatly appreciated. No hydrocracked products were tested. Jim Elder of the Mid-Continental Chemical Co. in DeSoto, KS, provided the pour-point depressants. The U-13 and T-20 cetane number refer-

ence fuels were donated by Phillips Petroleum. Biodiesel was donated by the National Biodiesel Board. Analytical support was provided by Todd Williams and KU's Department of Chemistry. Ying Rui assisted with laboratory procedures that made this work possible. Funding was provided by a grant from The University of Kansas Energy Research Center.

Literature Cited

- Agee, K. L.; Agee, M. A.; Willingham, F. Y.; Trepper, E. L. *Economical Utilization of Natural Gas to Produce Synthetic Petroleum Liquids*. GPA Convention Paper, March 1996.
- Allard, L. N.; Hole, N. J.; Webster, G. D.; Ryan, T. W., III; Ott, D.; Bergsazay, A.; Fairbridge, C. W.; Cooley, J.; Mitchell, K.; Richardson, E. K.; Elliot, N. G.; Rickard, D. J. *Diesel fuel ignition quality as determined by the Ignition quality tester (IQT)*; SAE Paper 971636; SAE: Warrendale, PA, 1996; Part II.
- Allard, L. N.; Webster, G. D.; Hole, N. J.; Ryan, T. W., III; Ott, D.; Fairbridge, C. W. *Diesel Fuel Ignition Quality as Determined in the Ignition Quality Tester (IQT)*; SAE Paper 961182; SAE: Warrendale, PA, 1997.
- Beatrice, C.; Bertoli, C.; Giacomo, N. D. *The Influence of Fuel Formulations on Pollutant of a Light Duty DI Diesel Engine*; SAE Paper 961972; SAE: Warrendale, PA, 1996.
- Bertoli, C.; Giacomo, N. D.; Iorio, B.; Prati, M. V. *The Influence of Fuel Composition on Particulate Emissions of DI Diesel Engines*; SAE Paper 932733; SAE: Warrendale, PA, 1993.
- Botros, M. *Enhancing the Cold Flow Behavior of Diesel Fuels*. SAE Paper 972899; SAE: Warrendale, PA, 1997.
- Callison, J. Amoco Quality Assurance Technical Department, 1997.
- Clothier, P.; Aguda, B.; Moise, A.; Pritchard, H. *How Do Diesel-Fuel Improvers Work?* *Chem. Soc. Rev.* 1993, 101.
- Davies, P. *Opportunities for Gas Conversion in the Middle East*. Middle East Petroleum and Gas Conference, 1997; p 1.
- Dean, J. A. *Lange's Handbook of Chemistry*, 13th ed.; McGraw-Hill: New York, 1985.
- Gerpen, J. V.; Yu, L.; Hammond, E. G.; Monyem, A. *The Influence of Contaminants on Biodiesel Properties*; SAE Paper 971685; SAE: Warrendale, PA, 1997.
- Henly, T. J. *New Equations to Predict Diesel Fuel Cetane Number*; SAE Paper 972897; SAE: Warrendale, PA, 1997.
- Marano, J. J.; Holder, G. D. *General Equation for Correlating the Thermophysical Properties of n-Paraffins, n-Olefins, and Other Homologous Series. 2. Asymptotic Behavior Correlations for PVT Properties*. *Ind. Eng. Chem. C Res.* 1997a, 37, 1895.
- Marano, J. J.; Holder, G. D. *Prediction of Bulk Properties of Fischer-Tropsch Derived Liquids*. *Ind. Eng. Chem. Res.* 1997b, 37, 2409.
- Mikkonen, S.; Kiskki, U.; Mäkelä, M.; Niemelä, A.; Niemelä, M.; Rantanen, L.; Salonen, P. *Reformulated Diesel Fuel-Four Years in Finland*; SAE Paper 971634; SAE: Warrendale, PA, 1997.
- Owen, K.; Coley, T. *Automotive Fuels Reference Book*, 2nd ed.; Society of Automotive Engineers, Inc.: Warrendale, PA, 1995.
- Peckman, J. *Diesel Fuel News*; Hart Publications Inc.: Potomac, MD, July 1997a; Vol. 1, No. 13, p 5.
- Peckman, J. *Diesel Fuel News*; Hart Publications Inc.: Potomac, MD, July 1997b; Vol. 1, No. 14, p 7.
- Peckman, J. *Premium Diesel Task Force Agrees on Five Fuel Properties. Growing Your Business with Premium Diesel*; Hart Publications International, Inc.: Potomac, MD, Jan 1998.
- Ryan, T. W.; Stapper, B. *Diesel Fuel Ignition Quality as Determined in a Constant Volume Combustion Bomb*; SAE Paper 870586; SAE: Warrendale, PA, 1987.
- Sandler, S. I. *Chemical and Engineering Thermodynamics*; John Wiley & Sons: New York, 1989.
- Schaberg, P. W.; Myburgh, I. S.; Botha, J. J.; Roets, P. N.; Viljoen, C. L.; Duncuart, L. P.; Starr, M. E. *Diesel Exhaust Emissions using Sasol Slurry Phase Distillate Process Fuels*. Comments made during presentation of paper at SAE Fall Fuels and Lubricants Conference, Tulsa, OK, Oct 14, 1997; SAE Paper 972898.
- Schwartz, M. M. *Selective Catalytic Cracking of Fischer-Tropsch Liquids to High Value Transportation Fuels*. Report number 38: Quarterly technical status report for fourth quarter fiscal

- year 1993, DOEPC90057T8; U.S. Department of Energy: Pittsburgh, PA, 1993.
- Suppes, G. J.; Rui, Y.; Rome, A. C.; Chen, Z. Cetane Improver Analysis and Impact of Activation Energy on Relative Performance of 2-Ethylhexyl Nitrate and Tetraethylene Glycol Dinitrate. *Ind. Eng. Chem. Res.* 1997a, 37, 4397.
- Suppes, G. J.; Rui, Y.; Regehr, E. V. *Hydrophilic Diesel Fuels—Ignition Delay Times of Several Different Blends*, SAE Paper 971686; SAE: Warrendale, PA, 1997b.
- Thompson, A. A.; Lambert, S. W.; Mulqueen, S. C. *Prediction of Precision of Cetane Number Improver Response Equations*, SAE Paper 972901; SAE: Warrendale, PA, 1997.
- Walas, S. M. *Phase Equilibrium in Chemical Engineering*; Butterworth-Heinemann, Stoneham, MA, 1985.
- Wuebben, P.; Unnasch, S.; Pellegrin, V.; Quigg, D.; Urban, B. *Transit Bus Operation with a DDC 6V-92TAC Engine Operating on Ignition-Improved Methanol*, SAE Paper 902161; SAE: Warrendale, PA, 1990.

Received for review October 27, 1997

Revised manuscript received February 12, 1998

Accepted February 24, 1998

IE970746E